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PtPdCo ternary electrocatalyst for methanol tolerant oxygen reduction reaction in direct methanol fuel cell



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ABSTRACT

Carbon-supported PtPdCo/C ternary electrocatalysts were prepared by using the sodium borohydride method for use as a cathode catalyst in direct methanol fuel cells (DMFCs). The electrocatalyst particles with a size of 2–3 nm were uniformly dispersed on carbon supports. PtPdCo/C showed a similar performance compared to commercial Pt/C in the oxygen reduction reaction (ORR) tests conducted with a rotating disk electrode (RDE). On the other hand, PtPdCo/C showed higher methanol tolerance than Pt/C in acidic media with methanol. In the single-cell tests, the performance of the PtPdCo/C electrocatalyst was approximately 50% higher than that of Pt/C owing to its enhanced methanol tolerance. In the long-term operation test with the single-cell, the maximum power density of PtPdCo/C decreased only by 14% from its initial value. These results indicate that the PtPdCo/C catalyst is potentially an alternative electrocatalyst for the cathode in DMFCs.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted significant attention as a portable power source owing to their advantages such as high energy efficiency, low operating temperature, and a simple configuration without the need for a reformer [1–3]. Despite these advantages, there are several obstacles that need to be overcome to achieve their commercialization, such as poor kinetics of the anode and cathode reaction, performance degradation during long-term operation, and crossover of methanol from the anode to the cathode through the polymer electrolyte membrane. In particular, as a result of the methanol crossover, the actual efficiency and performance of DMFCs are lower than theoretical values because of a mixed potential induced by the methanol oxidation reaction (MOR) and the oxygen reduction reaction (ORR) at the cathode [3–5].

To overcome these problems, there have been two main attempts over the last few decades: achieving higher catalytic activity for the ORR compared to Pt/C and more selective activation to methanol. These goals have been mainly obtained by the modification of the structure and composition of the catalyst, which are major factors in determining the adsorption and catalytic properties for an electrochemical reaction. In particular, Pt-based alloy catalysts with transition metals have been reported to exhibit enhanced ORR activity resulting from their unique electronic and geometric structures. For instance, PtCo/C, PtNi/C, PtFe/C, and PtCr/C were all employed as a cathode electrocatalyst in proton exchange membrane fuel cells (PEMFCs) and DMFCs [6-11]. On the other hand, recent studies examined Pd-based alloy catalysts as cathode electrocatalysts because of their good ORR activity and methanol tolerance properties [12–20]. Generally, the activity enhancement of Pd-based alloy catalysts for the ORR can be related to the changes in structural parameters. In the case of PdCo/C and PdFe/C, the ORR activities of the prepared catalysts were similar to that of Pt/C in PEMFCs [12,14]. In particular, PdCo catalysts were examined as a methanol tolerant cathode catalyst in DMFCs. In the presence of methanol, the PdCo/C catalysts showed higher ORR activity than Pt/C because of the lower activity of Pd for the MOR [16-24]. Nonetheless, two-component catalysts suffer from metal dissolution. The fabrication of multi-component catalysts is a promising approach not only to overcome the dissolution but also

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to improve the stability of electrocatalysts [2]. This is an important but difficult task, because a number of studies on the cathode catalysts for DMFCs have failed to perform actual full cell tests such as the single cell test; performance degradation was likely to occur during long-term operation [25–28].

In this study, multi-component catalysts such as PtPdCo/C ternary electrocatalysts were prepared and their ORR activity was evaluated in acidic media with and without methanol by the RDE technique. Additionally, the single cell performance with the synthesized PtPdCo/C catalysts was carefully examined for potential application to an actual DMFC system. Finally, long-term operation tests were successfully carried out to assess the durability of the single cell with the PtPdCo/C catalyst.

2. Experimental

2.1. Preparation of the electrocatalysts

Pt₃₅Pd₃₅Co₃₀/C and Pt₅₀Pd₅₀/C nanoparticles (60 wt%) were synthesized by the conventional sodium borohydride reduction method. First, the required amounts of carbon materials (Vulcan XC-72R, Cabot) were dispersed in distilled water, and then, adequate amounts of the Pt salt (H_2 PtCl₆·xH₂O, Aldrich Chem. Co.), Pd salt (Pd(NO₃)₂·xH₂O, Aldrich Chem. Co.) were added to the solution. After mixing the solutions, the metal salts were reduced by NaBH₄. The prepared materials were washed with distilled water and dried in a vacuum oven at 70 °C.

2.2. Physical characterization of the electrocatalysts

X-ray diffraction (XRD) analyses of the prepared catalysts were carried out with an X-ray diffractometer (Rigaku D/MAX 2500) using a CuK α source at 40 kV and 100 mA. The samples were scanned from 20° to 80° with a scanning rate of 2° min $^{-1}$. X-ray photoelectron spectra (XPS) were obtained using an Al K α source (ESCALAB 250 XPS spectrometer, VG Scientifics). Binding energies were calibrated with respect to the C (1s) peak at 285 eV. Experimental data were curve-fitted using AVANTAGE 4.19 software. High-resolution transmission electron microscopy (HR-TEM, JEOL 2010) was employed to examine the particle size and dispersion of the synthesized catalysts.

2.3. Electrochemical characterization of the electrocatalysts

The electrochemical measurements were done using an Autolab general-purpose electrochemical system (Eco Chemie). Glassy carbon electrodes (5 mm diameter) were coated with catalyst inks for use as the working electrode, and Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All potentials are quoted with respect to a reversible hydrogen electrode (RHE). To examine the effect of the prepared catalysts on the CO tolerance, CO stripping experiments were conducted in 0.5 M H₂SO₄. First, CO was adsorbed on the catalysts while maintaining the potential at 0.1 V for 20 min by bubbling CO gas into the solution. After the adsorption of CO, the CO gas was replaced with Ar gas to reduce the remaining CO in the solution while holding the potential at 0.1 V for 40 min. Then, the potential was varied from $0.1\,V$ to $1.2\,V$ at $20\,mV\,s^{-1}$ to record the CO stripping voltammograms. The ORR activities and methanol tolerances of the catalysts were measured using a rotating disk electrode (RDE) in 0.5 M H₂SO₄ and 0.5 M H₂SO₄ with 0.5 M CH₃OH saturated with oxygen gas at 25 °C. Linear sweep voltammetry was performed from 1.0 to 0.2 V vs. a reference hydrogen electrode with a scan rate of 5 mV s^{-1} at a rotation rate of 2500 rpm.

To test the single cell performance of the prepared catalysts, membrane electrode assemblies of the catalyst-coated membrane (CCM) type were fabricated. The anode catalyst layer was prepared using $4\,\mathrm{mg\,cm^{-2}}$ of PtRu black (Johnson Matthey) and the cathode catalyst layer was prepared using $3\,\mathrm{mg\,cm^{-2}}$ of Pt/C, PtPd/C and PtPdCo/C with an appropriate weight percent of an ionomer (5 wt% Nafion solution, Aldrich Chem. Co.). Membrane-electrode-assemblies (MEAs) of the CCM type was prepared by spraying the catalyst ink onto both sides of a Nafion 115 membrane that had been treated with a 3 wt% solution of $\mathrm{H_2O_2}$ for 1 h and then a 0.5 M solution of $\mathrm{H_2SO_4}$ for 1 h.

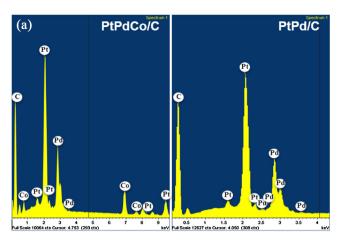
The single cell performance of each MEA was measured with the geometric area being 5 cm². The MEA was placed between two gas diffusion layers (GDLs) and inserted into graphite plates that contained serpentine flow channels. Using the same pressure as that at the moment of setting the cell, the single cell was assembled by means of a torque wrench. The single cell was then connected to a fuel cell test station (FCTS, WonATech Co., Ltd.). Methanol solution and air with flow rates of 2 ml min⁻¹ and 100 ccm were fed into the anode and cathode sides of the single cell, respectively, to measure the performance of the MEA. The temperature of the single cell was maintained at 55 °C. For the measurement of the long-term durability of the cells with the prepared catalysts, the single cell was discharged at a constant current density of 100 mA cm⁻² using 0.5 M methanol solution and air. The polarization curves were obtained every 250 h to measure the performance degradation. The long-term operation test was conducted at 55 °C for 1000 h.

3. Results and discussion

3.1. Physical characterization of the electrocatalyst

The chemical compositions of the synthesized PtPdCo/C and PtPd/C catalysts were evaluated using energy dispersive X-ray spectroscopy (EDX) and the corresponding results are shown in Fig. 1a. The atomic ratios of Pt:Pd:Co in the PtPdCo/C and Pt:Pd in the PtPd/C catalysts, which corresponded to the expected nominal values, were 35.1:35.4:29.5 and 49.9:50.1, respectively. The XRD patterns of the PtPd/C and PtPdCo/C catalysts are shown in Fig. 1b. In all cases, the XRD profiles of the prepared catalysts reveal a facecentered cubic structure. The XRD patterns of PtPdCo/C do not show any peaks of Co or Co oxides. However, their presence cannot be ruled out, because the Co particles may be of significantly small size and be present in a small amount or even in an amorphous form. The diffraction peaks of PtPdCo/C were slightly shifted to a higher angle compared to those of PtPd/C (from 39.81° to 40.04° for (1 1 1) peak, inset of Fig. 1b). These angle shifts of PtPdCo/C suggest the formation of an alloy of Pt, Pd, and Co. The mean crystallite sizes of the catalysts were estimated from the Debye-Scherrer equation using the (220) peaks, and were determined to be approximately 2.8 and 2.5 nm for PtPd/C and PtPdCo/C, respectively.

The prepared PtPd/C and PtPdCo/C catalysts were characterized by HR-TEM to investigate the size and dispersion of the nanoparticles, and the results are shown in Fig. 2. The PtPd and PtPdCo alloy particles are well dispersed on the carbon support without any major agglomeration, as shown in Fig. 2a and d, respectively. The spherical shapes and narrow distributions of the PtPd and PtPdCo alloy particles are also confirmed, as shown in Fig. 2b and e, respectively. Fig. 2c and f shows the particle size distribution histograms on the basis of approximately 300 alloy nanoparticles that were well dispersed on the surface of carbon. The average particle sizes of the PtPd/C and PtPdCo/C catalysts obtained by HR-TEM are approximately 2.6 and 2.4 nm, respectively, which are in good agreement with the XRD results.



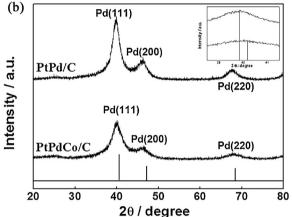


Fig. 1. (a) EDX patterns and (b) XRD of PtPd/C and PtPdCo/C catalysts. Inset of (b): detail of (1 1 1) peak.

Fig. 3 presents the XPS spectra of the electrocatalysts, showing the Pt 4*f* regions. The oxidation states of the commercial Pt/C (Fig. 3a), PtPd/C (Fig. 3b) and PtPdCo/C (Fig. 3c) catalysts are observed in a similar manner and the Pt atoms are mostly in the

Table 1Binding energy and atomic ratios of the Pt oxidation state for the Pt/C, PtPd/C, and PtPdCo/C spectra.

Material	Oxidation states (Pt $4f_{7/2}$)	Peak binding energy (eV)	Ratio (%)
- wideCitai	Oriention states (1 t 4)/ _[2]	reak binding chergy (cv)	14410 (70)
Pt/C	Pt (0)	71.87	65.59
	Pt (II)	72.92	26.50
	Pt (IV)	75.84	7.91
PtPd/C	Pt (0)	72.06	65.82
	Pt (II)	73.33	26.94
	Pt (IV)	75.17	7.24
PtPdCo/C	Pt (0)	71.96	66.29
	Pt (II)	73.31	26.56
	Pt (IV)	75.99	7.15

metallic form of Pt(0) (Table 1), which agrees well with previous literature reports [16]. There is a slight shift toward a higher energy in the Pt $4f_{7/2}$ peak of the PtPd/C and PtPdCo/C catalysts by approximately 0.19 eV and 0.09 eV, respectively, compared to that of the Pt/C catalyst (Fig. 3d). Such shifts could be associated with the change in Pt oxidation states, metal–metal interaction, Pt–carbon interactions, or small cluster-size effects [2,6]. However, the metal–metal interaction mechanism is the only plausible reason for the peak shift of Pt $4f_{7/2}$, given that the Pt oxidation states between the catalysts are similar and the unlikelihood of Pd or Co influencing the Pt–carbon interactions. This should also indicate a change in the electronic structure of Pt when it is alloyed with Pd and Co.

3.2. Electrochemical characterization of the electrocatalysts

CO poisoning in the cathode by methanol crossover causes a decrease in the DMFC performance because of the adsorption of CO on the catalyst surface. Therefore, CO resistance is one of the most important factors to improve the DMFC performance [5]. The CO stripping voltammograms of the PtPd/C, PtPdCo/C, and commercial Pt/C catalysts are shown in Fig. 4. The onset potentials and main peaks of CO oxidation move to higher positive values with increasing Pd content in the prepared catalysts. This result suggests that PtPd/C and PtPdCo/C have better CO resistance than Pt/C because of the presence of Pd in the catalysts [22]. The electrochemically

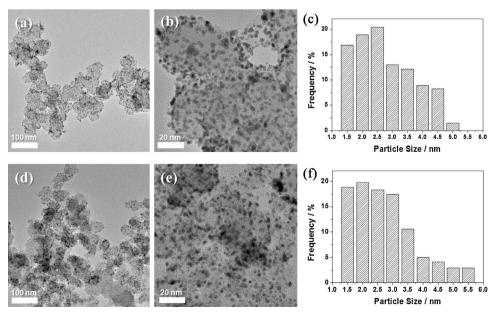


Fig. 2. HR-TEM images and particle size distribution histograms of PtPd/C and PtPdCo/C catalysts: (a) PtPd/C at low magnification, (b) PtPd/C at high magnification, (c) particle size distribution histograms of PtPd/C, (d) PtPdCo/C at low magnification, (e) PtPdCo/C at high magnification, and (f) particle size distribution histogram of PtPdCo/C.

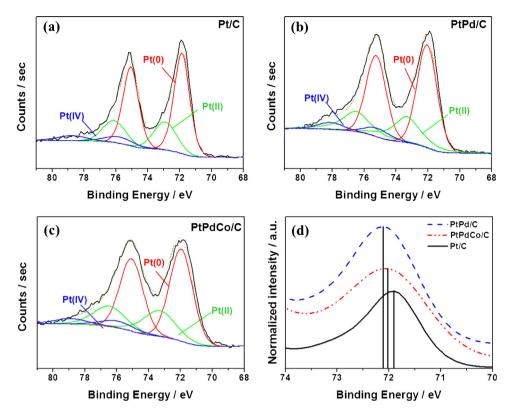


Fig. 3. XPS spectra of Pt 4f peak for (a) Pt/C, (b) PtPd/C, (c) PtPdCo/C catalysts, and (d) detail of the Pt 4f_{7/2}.

active surface area (ECSA) is one of the most important parameters for catalytic activity. The actual surface area of Pt-based catalysts is generally estimated from the integrated charge of the hydrogen adsorption region in the cyclic voltammograms (CV). However, for multi-component catalysts such as Pd alloys, the ECSA values were needed to be calculated using the CO stripping result because the Pd metal absorbs hydrogen and thus, the hydrogen adsorption region may not be estimated precisely. The ECSA values of the PtPd/C, PtPdCo/C, and commercial Pt/C catalysts determined from the CO stripping voltammograms were 36.37 m² g⁻¹, 22.28 m² g⁻¹, and 27.81 m² g⁻¹, respectively, which suggests that those ECSA values increase with the Pd content in the catalyst. However, the potential influence of particle size difference and degree of aggregation,

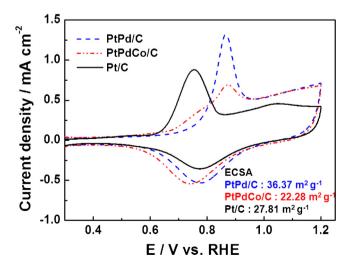
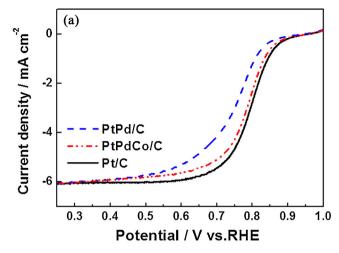


Fig. 4. CO stripping voltammograms of the PtPd/C, PtPdCo/C, and commercial Pt/C catalysts in $0.5 \, M \, H_2 SO_4$ at a sweep rate of $20 \, mV \, s^{-1}$.

and the relation between ECSA and Pd content are not yet clearly understood.

To evaluate the catalytic activity for the ORR and methanol tolerance of the prepared catalysts, linear sweep voltammetry was performed using an RDE at 2500 rpm in oxygen-saturated 0.5 M H₂SO₄ with and without methanol. Fig. 5a displays the linear sweep voltammograms of the PtPdCo/C and PtPd/C catalysts. The voltammogram of the commercial, 60 wt% Pt/C (Johnson Matthey) catalyst is also included for comparison. In the absence of methanol, the ORR activities of the PtPdCo/C and PtPd/C catalysts are similar to each other but slightly lower than that of Pt/C, with the half-wave potential value of PtPdCo/C being more positive than that of PtPd/C. This result suggests that the addition of Co might have a positive effect on the ORR in a PtPd/C system. This is because the Pt and Pd lattices were compressed by alloying with Co, changing the electronic states. Although there is no direct evidence implying that the d-band center of the alloy was shifted to a lower value, it can be inferred indirectly through the change in the Pt $4f_{7/2}$ binding energy from the XPS, Pd peak shift in the XRD, and enhanced ORR activity of both the half- and single-cells. In multi-component systems, such as PtM₁M₂/C, the d-band center may shift because of a strain effect (caused by the lattice mismatch in the multi-component system), lowering the adsorption energy of the surface oxygenated intermediate, and thus, the surface catalytic activity is enhanced [17]. Xiaowei and coworkers reported that Pd-Co/C catalysts have higher ORR mass activities than Pd/C catalysts due to the more favored oxygen adsorption on the catalyst surface [18]. Fig. 5b shows the linear sweep voltammograms of the PtPdCo/C and PtPd/C catalysts in O_2 saturated $0.5\,M$ H_2SO_4 with $0.5\,M$ methanol at $2500\,rpm$. The voltammogram of the commercial 60 wt% Pt/C catalyst is also included for comparison in the presence of methanol. The linear sweep polarization curve of PtPd/C in the presence of methanol is similar to that of PtPd/C without methanol, while the PtPdCo/C catalyst in the presence of methanol displays a plateau at 0.7 V due to the mixed current of the ORR and MOR. Conversely, the



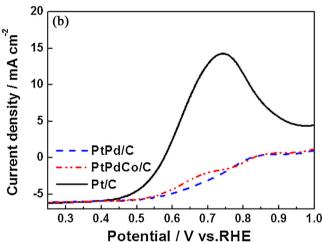


Fig. 5. Polarization curves for the ORR on PtPd/C, PtPdCo/C and commercial Pt/C catalysts recorded in (a) O_2 saturated $0.5\,\mathrm{M}$ H₂SO₄ and (b) $0.5\,\mathrm{M}$ H₂SO₄ with $0.5\,\mathrm{M}$ methanol at room temperature, obtained using a rotating disk electrode at 2500 rpm and a sweep rate of $5\,\mathrm{mV}\,\mathrm{s}^{-1}$.

commercial Pt/C catalyst shows the MOR but no plateau in this region. These results indicate that the PtPdCo/C and PtPd/C catalysts possess superior methanol tolerance to commercial Pt/C. It is well known that Pd itself is not only inactive, but also does not show any activity even with the addition of Co for the adsorption and oxidation of methanol [19]. In theory, the structure and composition of the catalyst requires a minimum of three active Pt sites nearby for methanol oxidation. Yet, in the presence of both Pd and Co atoms on the catalyst surface, methanol adsorption on the catalyst surface is unlikely in most cases because there are not a sufficient number of active Pt sites nearby on the surface of the Pt-Pd-Co alloy system. Nevertheless, the ORR activity of the Pt alloy catalyst is not seriously hindered by such alloying. Since only two Pt sites are required for oxygen adsorption and these two adjacent Pt sites are plentifully available on the surface of the alloy [16-23], both Pd and Co in the PtPdCo/C and PtPd/C catalysts play a key role in the inactivation of methanol adsorption and oxidation at the cathode. These conceptions for methanol tolerance and ORR activities of PtPdCo/C catalysts are well represented in conceptual diagrams

For a bimetallic catalyst system, this phenomenon is well known as 'ensemble effect', which occurs when the active component is diluted by catalytically inert metals forming a bimetallic catalyst that causes changes in the distribution of active sites and opens different reaction pathways [24]. Therefore, the effects of Pt and

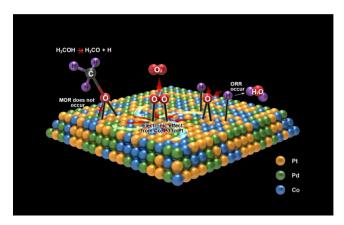


Fig. 6. Conceptual diagram of the PtPdCo/C cathode surface during the methanol adsorption and oxidation.

Co in the PtPdCo/C catalyst on the MOR may be responsible for the plateau in Fig. 5b.

To test the prepared catalysts in an actual DMFC system, MEAs of the CCM type were fabricated using the synthesized catalysts as the cathode. Fig. 7 shows a comparison of the single cell performance using PtPdCo/C, PtPd/C, and commercial Pt/C as the cathode catalyst. For this experiment, 0.5 M methanol and air were fed into the anode and cathode, respectively. The open circuit voltages (OCVs) of the MEA with PtPdCo/C, PtPd/C, and Pt/C were 0.81 V, 0.79 V, and 0.75 V, respectively. The maximum power density of the MEA with PtPdCo/C was similar to that of the MEA with commercial Pt/C with both showing approximately 40 mW cm⁻² at 0.36 V, whereas that of the MEA with PtPd/C was 33 mW cm⁻² at 0.26 V. It is noteworthy to point out that the single cell performance trend observed in Fig. 7 is similar to that of the ORR activity demonstrated in Fig. 5a. This implies that the catalytic activity of the ORR has more influence on the performance of the DMFC than the methanol tolerance at a low concentration of methanol because of the small amount of methanol crossover.

Fig. 8a and b displays the polarization curves of the single cells with the PtPdCo/C (a) and commercial Pt/C catalysts (b) as the cathode, respectively, with various methanol concentrations. To investigate the effect of the methanol concentration on the performance of the DMFC, the feeding concentration of methanol was changed from 0.5 M to 3.0 M. As shown in Fig. 8a, the polarization curves of the MEA with the PtPdCo/C catalyst exhibit a similar

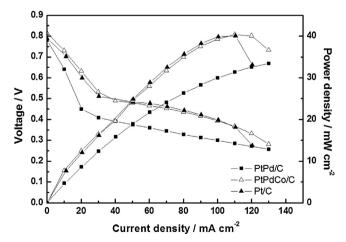


Fig. 7. Polarization and power density curves of PtPd/C, PtPdCo/C and commercial Pt/C catalysts used as the cathode in DMFCs at 55° C with a metal loading of 3 mg cm⁻². The anode catalyst was a commercial PtRu black (Johnson Matthey). The PtRu loading in the anode was 4 mg cm⁻².

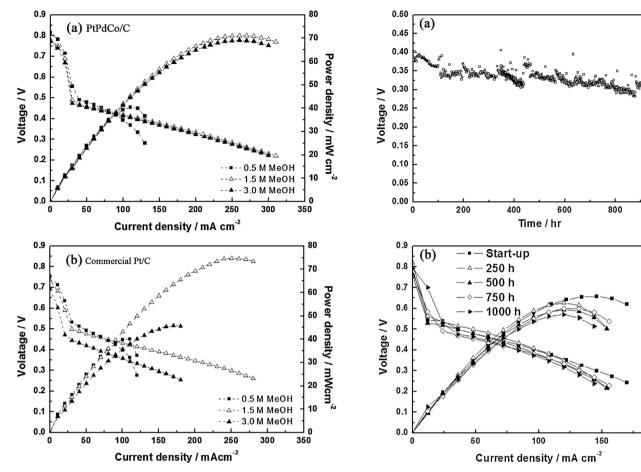


Fig. 8. Polarization and power density curves of (a) PtPdCo/C and (b) commercial Pt/C catalysts used as the cathode in DMFCs at 55 °C with differing concentrations of methanol into the anode.

Fig. 9. Long-term operation test of the single-cell with the PtPdCo/C catalyst as the cathode in the DMFC: (a) variation of the cell potential with time at a constant current density of 100 mA cm⁻² and (b) polarization and power density curves at various periods of time during operation at a constant current density.

1000

60

50

40

200

tendency to those of the commercial Pt/C in methanol at concentrations ranging from 0.5 M to 1.5 M. However, the polarization curve in 3.0 M methanol is similar to that in 1.5 M methanol, although the amount of methanol crossover increases with increasing methanol concentration. The OCVs of the cells with PtPdCo/C as the cathode catalyst were 0.81 V, 0.78 V, and 0.77 V with 0.5 M, 1.5 M, and 3.0 M methanol, respectively, all of which are higher than those of the cells with the commercial Pt/C.

However, as shown in Fig. 8b, the performance of the MEA with commercial Pt/C increases with increasing methanol concentration from 0.5 M to 1.5 M. On the other hand, the single cell performance slightly decreases when the methanol concentration increases from 1.5 M to 3.0 M. It is inferred from this result that the methanol oxidation at the anode increased, as did the methanol crossover from the anode to the cathode. The methanol crossover causes an increase in the mixed potential at the cathode, and consequently, the performance of the single cell decreased with further increasing methanol concentration. The OCVs of the MEA with Pt/C were 0.75 V, 0.73 V, and 0.69 V when 0.5 M, 1.5 M, and 3.0 M methanol was respectively fed into the anode. The decrease of the OCV with increasing methanol concentration is attributed to the increase in the amount of methanol crossover.

The maximum power density of the MEA with PtPdCo/C using $3.0\,\mathrm{M}$ methanol was $69\,\mathrm{mW\,cm^{-2}}$, which is 50% higher than that of the MEA with Pt/C ($46\,\mathrm{mW\,cm^{-2}}$) under the same conditions. These results are attributed to the higher methanol tolerance of the MEA with the PtPdCo/C catalyst compared to that of the MEA with commercial Pt/C.

Fig. 9a shows the cell voltage at $100\,\text{mA}\,\text{cm}^{-2}$ during the long-term operation test performed for $1000\,\text{h}$. The degradation rate of the single cell is approximately $80\,\mu\text{V}\,\text{h}^{-1}$ at a constant current density. The polarization curves obtained from the long-term operation test exhibit performance degradation only by 14% from 0 h to $1000\,\text{h}$, as shown in Fig. 9b. Comparison of this result with commercial Pt/C which reported previous literature [25,26] reveals a higher stability of PtPdCo/C catalyst than commercial Pt/C under similar test condition. For this study, the performance degradation ratio is about 14%, however approximately 30% of the maximum power density was lost after the life test, for commercial Pt/C.

From the polarization curves in Fig. 9b, performance degradation was observed in the low potential region, suggesting that there is an increase in the mass transfer resistance caused by products such as water [26]. No significant performance degradation resulting from catalyst decay was observed. However, only one mechanism may not be solely responsible for the performance degradation. There are several well-known mechanisms that can account for the degradation of a DMFC in the single cell test, such as catalyst decay, the degradation of the membrane, and the transformation of the GDL and MPL [26–28]. The catalyst degradation mechanism is particularly interesting, but was not investigated in this study. It should be assessed in future studies by carrying out systematic physical and electrochemical analyses.

4. Conclusions

In this study, PtPdCo/C ternary electrocatalysts were prepared by the borohydride reduction method. The nano-sized particles of the PtPdCo/C catalysts were well dispersed on the carbon supports. The prepared catalysts exhibit similar ORR activity compared to commercial Pt/C and superior methanol tolerance in the half-cell test and the actual DMFC single-cell test. The long-term operation test was performed successfully, revealing that the maximum power density behavior of PtPdCo/C resulted in performance degradation only by 14% from 0 h to 1000 h. These results suggest that PtPdCo/C can be used as a replacement for the cathode catalyst in DMFCs.

Acknowledgments

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